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2,3,7,8-TCDD (2,3,7,8-Tetrachlorodibenzo -p-Dioxin): Environmental Chemistry

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2,3,7,8-TCDD: ENVIRONMENTAL CHEMISTRY

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16. ABSTRACT

For molecules of its size and weight, 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD) is one of the most toxic, least water soluble, least volatile, and most resistant to thermal and biological transformations. The combination of these properties has presented a challenging problem is assessing human hazards ascribable to TCDD because, although exposure concentrations are often low, the time frame for transport and most degradative processes in the environment is generally long. Under normal environmental conditions, the only transformation process that is fairly rapid for dioxins is photolysis.

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2,3,7,8-TCDD: Environmental Chemistry

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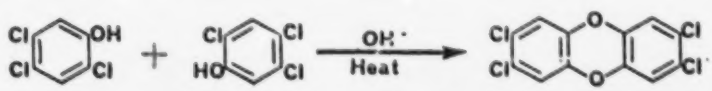
For molecules of its size and molecular weight, 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD) is one of the most toxic, least water soluble, least volatile, and most resistant to thermal and biological transformations. The combination of these properties has presented a challenging problem in assessing human hazards ascribable to TCDD because, although exposure concentrations are often low, the time frame for transport and most degradative processes in the environment is generally long. Under normal environmental conditions the only transformation process that is fairly rapid for dioxins is photolysis.

This introductory chapter is designed to provide a general background on the environmental transformation and transport of TCDD, with emphasis on its environmental chemistry. It is not a complete review of the substantial amount of literature available on the topic, but is meant to set the stage for the following papers that discuss certain aspects of this subject in greater detail.

2,3,7,8-TCDD is a symmetrical molecule, generally synthesized by the condensation of two molecules of 2,4,5-trichlorophenol in the presence of base at high temperatures (1).



2,4,5-trichlorophenol 2,3,7,8-TCDD

An abbreviated list of its physicochemical properties is given in Table I. A more complete list of other properties is presented by

Schroy and co-workers (2). Because of the extreme character of many of these properties, refinement of these values is an ongoing process. Reports on improved measurements of water solubility and vapor pressure were recently published (3,5).

Table I. Selected Chemical and Physical Properties of 2,3,7,8-TCDD

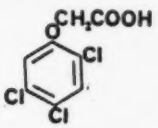
Property		Reference
Molecular weight	321.974	
Vapor pressure		
(25° C)	$7.4 + 0.4 \times 10^{-10}$ torr	(3)
(30° C)	3.46×10^{-9}	(2)
(54.6° C)	1.37×10^{-7}	(2)
(71° C)	1.19×10^{-6}	(2)
Melting point	305.0° C	(4)
Solubility in:		
(all at 25° C)		
water	19.3 nanograms/liter	(5)
benzene	570 milligrams/liter	(6)
methanol	10 milligrams/liter	(6)
acetone	110 milligrams/liter	(6)
Partition coefficient	1.4×10^{6}, 3.0×10^{8}	(7,8)
(octanol/water)	$(4.24 \pm 2.73) \times 10^{6}$	(5)
Molecular diffusivity:		
in air (calculated)	4.7×10^{-2} cm^2/s	(3)
in water (calculated)	5.1×10^{-6} cm^2/s	(3)
Photolysis quantum yields		
(313 nm)		
water-acetonitrile		
(90:10)	0.0022	(9)
hexane	0.049	(9)

Sources and Distribution

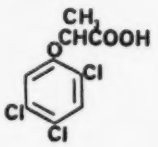
2,3,7,8-TCDD and related dioxins and dibenzofurans have come from two primary sources: (a) impurities in 2,4,5-trichlorophenol and related chemicals and (b) combustion processes. The products that have been manufactured from 2,4,5-trichlorophenol include herbicides such as 2-(2,4,5-trichlorophenoxy)propionic acid (silvex), 2,3,5-trichlorophenoxyacetic acid (2,4,5-T), and the disinfectant hexachlorophene (10). As discussed above, 2,3,7,8-TCDD is produced as a byproduct when 2,4,5-trichlorophenol is synthesized, and is found in significant concentrations in the synthesis residue (still bottoms). Chemical wastes containing 2,3,7,8-TCDD have been released directly into the environment. In some cases it has migrated from chemical waste dumps. For example, sediment samples taken near the Love

Canal site in New York contained 0.9-312 ppb 2,3,7,8-TCDD, which presumably originated at a chemical waste dump (11). 2,3,7,8-TCDD was also spread over wide areas in Missouri when 2,4,5-trichlorophenol waste was incorporated into waste oil and used to control dust on roads, parking lots and horse arenas. The estimated volume of contaminated Missouri soil ranged from 150,000 to 400,000 cubic meters (12).

Agricultural and wartime use of trichlorophenol-based herbicides such as 2,4,5-T and silvex also has resulted in release of 2,3,7,8-TCDD at low concentrations in many countries.



2,4,5-T



silvex

These herbicides have been used extensively in silviculture for control of deciduous trees in conifer forests (13). As a military defoliant, 2,4,5-T was mixed with 2,4-dichlorophenoxy acetic acid (2,4-D), and an estimated 10 million gallons of this mixture was applied in South Vietnam under the name of Agent Orange. Subsequent analysis of human samples from South Vietnam has found 2,3,7,8-TCDD at elevated levels compared to samples from North Vietnam where Agent Orange was not used (14).

More recently, environmental contamination by chlorinated dioxins and furans released during combustion processes has been recognized. These substances are formed not only during incineration of chlorinated phenols, but also during combustion of materials in home fireplaces and municipal incinerators (10). Chlorinated dioxins and dibenzofurans also are formed during fires involving polychlorinated biphenyls (15).

Another potential source for the more toxic dioxin congeners is the photoreduction of the higher chlorinated dioxins, i.e. the octachloro and heptacholoro congeners, to the lower chlorinated isomers. There are conflicting results concerning which positions are photoreduced on the dioxin aromatic rings. If the 1,4,6,9-positions are most rapidly reduced, toxic tetra, penta and hexachloro isomers (2,3,7,8-substituted) may result. If, however, the lateral (2,3,7,8) positions are photoreduced, the resulting products are substantially less toxic. The available information on this question is mixed. Buser (16) observed that UV irradiation of solutions of octachlorodibenzo-p-dioxin (OCDD) resulted in preferential formation of 1,2,3,4,6,7,9-hepta-CDD, which indicates primary initial loss of the lateral (2,3,7,8) chlorines. This preferential loss of lateral chlorines was also observed by Dobbs and Grant (17). Alternatively, Lamparski and co-workers (18) report preferential loss of chlorine atoms from the 1,4,6,9-positions as the initial photoreduction of OCDD when irradiated on a wood surface. Cull and Dobbs (19) observed no preferential loss from either position. Both heptachloro

isomers were formed in similar yields. The reason for these differences remains unknown.

Because of their low water solubiliy and low volatility, 2,3,7,8-TCDD and related dioxins are predominantly sorbed on particles, particularly soils and sediments. Assessing exposure to these compounds requires the ability to predict their time-varying concentrations in those important environmental compartments. Both biological and non-biological transformation and transport processes must be considered, including hydrolysis, oxidation, reduction and phototransformation. For 2,3,7,8-TCDD, attempts have been made to model each process in several environmental systems, with varying degrees of success. Because of the toxicity of 2,3,7,8-TCDD, various model compounds have been utilized, particularly other chlorinated dioxins. Caution must be taken when extending these results to 2,3,7,8-TCDD, however, because this isomer is in many ways toxicologically and chemically unique. There is often only limited rationale for estimating the properties of 2,3,7,8-TCDD based on the behavior of other isomers, i.e. 1,4,6,9-TCDD.

Biological Transformations

In contrast to the profound effect that 2,3,7,8-TCDD can have on biological systems, most biological systems have little impact on 2,3,7,8-TCDD. Early studies by Matsumura and Benezet (20) demonstrated that microbial metabolism was very slow if it occurred at all. Further work confirmed that although 2,3,7,8-TCDD is indeed relatively stable to microbial metabolism, two isolated microorganisms that gave water soluble metabolites were identified. In both aquatic sediment and terrestrial soil systems, metabolism of 2,3,7,8-TCDD was demonstrated. Addition of nutrients such as glucose, mannitol, and bactopeptone stimulated the transformation (21).

Substantial microbial degradation of 2,3,7,8-TCDD in oxic environments has not been demonstrated in field studies. Biodegradation was sufficiently slow that essentially all of the originally applied 2,3,7,8-TCDD in an experimental plot at Eglin Air Force Base in Florida in 1972 was still there in 1985 (22). Kimbrough and coworkers (23), estimated that the half-life for polychlorinated dibenzodioxins in soils was 10 years. Over a short (20 day) period, Pocchiari (24) did not observe increased rates of microbial degradation of 2,3,7,8-TCDD in organic-nutrient-amended soils from Seveso, Italy.

In a model ecosystem using aquatic sediment and lake water, metabolism played only a minor role in the loss of 2,3,7,8-TCDD (25). Volatilization was suggested to be the major mode of disappearance in samples incubated 39 days or more. The half-life under the conditions of the experiment in this model ecosystem was on the order of 600 days. Microbial metabolism appeared to be enhanced when microbial growth was stimulated; under such conditions metabolites were observed. One organism which can degrade 2,3,7,8-TCDD at an appreciable rate is the white rot fungus, Phanerochaete chrysosporium (26). The ability of this fungus to metabolize 2,3,7,8-TCDD was suggested to be dependent on an extracellular ligin-degrading enzyme system.

The lack of appreciable metabolism of 2,3,7,8-TCDD in aerobic environments can in part be explained by the high oxidation state of

the molecule. The six electron withdrawing atoms on 2,3,7,8-TCDD reduce the ease of oxidative metabolism. Although the available information is not substantial, reduction may be as important as oxidation. Evidence exists that 2,3,7,8-TCDD may be slowly degraded by anaerobic microorganisms in an organic matrix used for secondary treatment of chlorophenolic wastewaters (27).

Further support that reduction may be important for 2,3,7,8-TCDD is provided by the observation that it undergoes reduction to the lower chlorinated isomers in electron impact mass spectrometry when hydrogen is used as the gas chromatographic carrier gas (28). In addition, degradation of 2,3,7,8-TCDD in basic solutions of polyethyleneglycol and oxidants actually appears to occur by reductive processes, since the products are the lower chlorinated dioxins (29).

Abiotic Transformation

Oxidation, Hydrolysis and Reduction. 2,3,7,8-TCDD is not susceptible to hydrolysis at environmental temperatures (3) and is highly stable to chemical oxidation. TCDD exhibits thermal stability at environmental temperatures. Indeed, the thermal stability of TCDD is such that temperatures of 1400°F to 2400°F are used for efficient (>99.9999%) degradation of 2,3,7,8-TCDD from contaminated soils (30). Reaction rates with hydroxyl radicals have not been measured, although Podoll and co-workers (3) estimated the vapor phase rate constant to be on the order of 3×10^{8} $M^{-1} s^{-1}$. Using average OH radical concentrations to be 3×10^{-15} M, a half life of 200 hours was estimated for oxidation of TCDD in the atmosphere.

Photodegradation. Of all the possible natural degradation mechanisms, photodegradation has been suggested to be the most significant (3,9,10,27). 2,3,7,8-TCDD undergoes rapid degradation when exposed to ultra-violet light in the presence of a hydrogen (reducing) source. The photochemistry of dioxins has been reviewed by Choudhry and Hutzinger (31) and Esposito and coworkers (27).

Dulin and coworkers (32) have measured the quantum yield for photolysis of 2,3,7,8-TCDD in an acetonitrile/water mixture and in hexane (Table I). The more than 20-fold difference in quantum yield confirms either the need for a hydrogen source for efficient photolysis, or that the reaction pathway is substantially altered on going to a largely water solvent. The absorption spectra of 2,3,7,8-TCDD in acetonitrile shows a strong band centered at 309 nm with an extinction coefficient of 7020 $M^{-1} cm^{-1}$, whereas in hexane the band is centered at 304 nm with extinction coefficient of 5640 $M^{-1} cm^{-1}$. For sunlight photolysis, the higher quantum yield in hexane may be partially offset by reduced spectral overlap of 2,3,7,8-TCDD with the solar spectrum. In hexane, under identical conditions, the quantum yield for photolysis of 2,3,7-trichlorodibenzo-p-dioxin was 0.20, which was over four times higher than for 2,3,7,8-TCDD. Using the photolysis quantum yield, Podoll and coworkers (3) determined that the photolysis half-lives in surface waters varied from 21 hours in summer to 118 hours in winter.

Choudhry and Webster (33) also found low quantum yields for photolysis of 1,2,3,4,7-pentachorodibenzo-p-dioxin and 1,2,3,4,7,8-hexachlorodibenzo-p-dioxin of 9.8×10^{-5} and 1.1×10^{-4}, respec-

tively in water:acetonitrile (4:6) solutions. Both of these solvents are poor hydrogen donors, evidenced by the low quantum yields. Assuming that the quantum yields are the same in pure water, half lives of both compounds are 15 and 6 days, respectively, for the compounds in summer sun at 40° N. Botre' and coworkers (39) found that 2,3,7,8-TCDD was most rapidly lost in micelles of 1-hexadecylpyridinium chloride ($t_{1/2}$ 4 hrs) compared to micelles of sodium dodecyl sulfate ($t_{1/2}$ 8 hrs) and methanol ($t_{1/2}$ 18 hrs). Unfiltered mercury lamps were used in these studies.

Nestrick and coworkers (34) observed a striking difference in the photolysis rates of a series of tetrachlorinated dibenzo-p-dioxins. 2,3,7,8-TCDD underwent the most rapid photolysis in hexadecane. The rate of photolysis was 148 times more rapid than that of the 1,4,6,9-TCDD isomer when exposed to light from an RS sunlamp. Other TCDD isomers had relative photolysis rates varying between 2.7 times slower (1,3,7,8-TCDD) to 24 times slower (1,3,6,9-TCDD). The problem with relating these results to outdoor conditions is that the overlap of the absorption spectra of each of the isomers with the emission spectra of the RS sunlamp was not considered (35). 2,3,7,8-TCDD has an absorption band at 310 nm (extinction coefficient of 5590) in chloroform (36). This wavelength is also near the most intense emission band (314-316 nm) of the RS sunlamp between 290 nm and 320 nm (34). Other tetrachlorinated isomers have absorption maxima at wavelengths different than 2,3,7,8-TCDD. Even with this consideration, the data support evidence by others that photolysis of TCDD isomers is most rapid for those substituted on the lateral (2,3,7,8) positions.

Alternatively, Nestrick and co-workers (34) showed that 2,3,7,8-TCDD was the most stable of the 22 TCDD isomers examined on glass. 1,4,6,9-TCDD was the second most stable TCDD isomer, with a relative half-life that was 0.099 times that of 2,3,7,8-TCDD. The isomer most photoreactive on the glass surface, 1,2,3,9-TCDD, exhibited a half-life that was 0.014 times that of 2,3,7,8-TCDD. RS sunlamps also were used in this study, and no correction was provided for different absorption spectra of the various isomers. Although quantum yields would be more interpretable, it is nonetheless surprising that 2,3,7,8-TCDD photodecomposed the most rapidly in solution, but most slowly when exposed to light on a glass surface.

Molecular orbital calculations of 2,3,7,8-TCDD and dibenzo-p-dioxin indicate that excitation of either molecule results in promotion of an electron into an anti-bonding orbital with electron density primarily located on the 2,3,7,8 positions, with only a small percentage on the 1,4,6,9 positions (37). The primary photoproducts of 2,3,7,8-TCDD in organic solvent has been suggested to be the 2,3,7-trichloro isomer and the dichloro isomers (38). These photoproducts also appear to photodegrade faster than 2,3,7,8-TCDD. No other photoproducts have been identified from the photolysis of 2,3,7,8-TCDD, except for a "yellow, non-volatile gum" that was formed after extended exposure of methanolic solutions to fluorescent lamps (38).

Alternatively, a recent study by Dulin and coworkers (9) found no photoproducts for 2,3,7,8-TCDD in either water or hexane, despite a careful analysis of the reaction solution for 2,3,7-trichlorodibenzo-p-dioxin. They suggested that cleavage of one Ar-O bond is an alternative photochemical pathway which may predominate during 2,3,

7,8-TCDD photolysis. This mechanism would not result in chlorine replacement by hydrogen and would account for their finding that lower chlorinated dioxins were not produced in detectable quantities.

All of the studies to date have consistently demonstrated that the photolysis rate of 2,3,7,8-TCDD is dependent on the chemical environment in which it resides. Organic solvents dramatically accelerate the photolysis rate. Crosby and coworkers (38) found that, although the half-life of 2,3,7,8-TCDD in methanol under fluorescent lamp irradiation was approximately 3 hours, irradiation on either a Norfolk sandy soil for 96 hours, or as a thin dry film on glass for 14 days showed no loss of 2,3,7,8-TCDD. Wipf and coworkers (39) state that the photolysis rate of 2,3,7,8-TCDD on vegetation is increased by a factor of 25 when olive oil or arachis oil is used as a hydrogen source.

Photolysis of 2,3,7,8-TCDD on soil surfaces has been most studied to date by Liberti and coworkers (40). Their goal was to find methods to accelerate the loss of 2,3,7,8-TCDD from contaminated soil in Seveso, Italy. Unfiltered, high pressure mercury lamps were used in these studies. An important finding in this work is that a temperature dependence on the photolysis rate of 2,3,7,8-TCDD on glass plates was observed. At 23° C the half-life was approximately 50 hours; at 30° C the half-life was approximately 9 hours. Increased volatilization may have accounted for part of the greater loss at the higher temperature. Most significantly, under controlled conditions at 1 cm depth in soils, nearly 100% of the 2,3,7,8-TCDD was lost after nine days of exposure to summer sunlight, with an added hydrogen donor of 1:1 v/v solution of xylene and ethyl oleate. In addition, 40-60% was lost in the "lower" layers, presumably 2-3 cm depth. The surprisingly high loss in the lower layers was suggested to be due to either diffusion of 2,3,7,8-TCDD in the oleate layer or to a "photolytic reaction occuring through radicals."

Crosby and Wong (41) examined the sunlight photolysis of 2,3,7,8-TCDD on glass surfaces using various 2,4,5-T formulations, including Agent Orange, the herbicide Esteron and Esteron formulation without 2,4,5-T. In sunlight, photolysis of 2,3,7,8-TCDD in Agent Orange resulted in nearly 60% loss of 2,3,7,8-TCDD in 6 hours. In the presence of the herbicide, Esteron, 70% was lost in 6 hours, and nearly 90% was lost in 2 hours of sunlight exposure in Esteron formulation without 2,4,5-T. 2,3,7,8-TCDD photolysis loss in Agent Orange also was examined on soil and rubber plant leaf surfaces. Loss was again rapid on the plant surface with 70 to 90% loss in 6 hours. On soils, photolysis was substantially slower and more than 80% of 2,3,7,8-TCDD remained after 6 hours of exposure. Rapid initial loss from the soil was followed by a pronounced decrease in the photolysis rate constant. On 2,3,7,8-TCDD contaminated soils treated with olive oil, photodecomposition also was observed in experiments at Seveso, Italy, although substantial data scatter was apparent (42).

Gebefugi and coworkers (43) irradiated 2,3,7,8-TCDD sorbed on silica gel with pyrex filtered high pressure mercury arc radiation and found that only 8% remained following 18 days of exposure. They concluded that photochemical decomposition of 2,3,7,8-TCDD in sunlight is likely in soils, even without an added organic solvent.

Plimmer (44) also found that 63% of 2,3,7,8-TCDD degraded on silica gel exposed to 20 hours of sunlight and produced a polar product. Only 68% of the original radioactivity was recovered after the 20-hour exposure, suggesting that volatility may be a factor in the loss. On soils, no difference was observed between exposed and non-exposed areas, suggesting that soil exerts a protective effect against the photolysis of 2,3,7,8-TCDD.

Exner and coworkers (45) have recently described a process of in-place detoxication of dioxin-contaminated soil using an unfiltered 450 watt mercury arc lamp. The goal of this work was to determine whether dioxin contaminated soils could be treated by exposure to intense ultraviolet light. As in other studies, an organic solvent greatly accelerated the process. Using Times Beach, Missouri soils, which were heavily contaminated, they demonstrated substantial reduction in the amount of 2,3,7,8-TCDD on the soils when various soil amendments were used. The soil depth in these experiments ranged from 4 to 8 mm and contained: (a) ethyl oleate/o-xylene sprayed at 0.35 L/m^2 (27 hour exposure gave 81% removal); (b) ethyl oleate/water surfactant (75-hour exposure gave 68% removal); and (c) aqueous surfactants at 2% w/w of the soils (7 hour exposure gave 63% removal). In the last experiment (3), irradiation of dry soils for 7 hours gave no detectable loss of 2,3,7,8-TCDD, and soils sprayed only with water and irradiated for 7 hours showed only 6% loss of 2,3,7,8-TCDD. Mixing and rewetting the soils with the organic solvent at 30-minute intervals during irradiation resulted in greater loss of 2,3,7,8-TCDD. In each of the experiments using aqueous surfactants, the soils were rewetted during the irradiation. The primary conclusion of this research was that in-place destruction of 2,3,7,8-TCDD occurs readily in the presence of 0.3-3% w/w levels of common agricultural surfactants. It also implied that solubilization and transport to the air/soil surface may be a necessary step for degradation of 2,3,7,8-TCDD by light.

Measurement of the vapor phase photolysis of 2,3,7,8-TCDD is experimentally a major challenge due to the low volatility. Podoll and coworkers (3), however, have estimated the half life of 2,3,7,8-TCDD in the vapor phase to be 55 minutes. This estimate assumed that the quantum yield is the same as in hexane and is invariant with wavelength, that the spectral properties are the same as in solution, and that the mechanisms for transformation are the same. This photolysis half-life is approximately 200 times smaller than that expected for reaction with hydroxyl radical. However, both vapor phase photolysis and reactions with OH radicals would be unimportant if TCDD is predominantly sorbed on particles in the atmosphere. Experimental verification of these estimates is needed, because atmospheric transformation may be an important fate of 2,3,7,8-TCDD and other dioxins which enter the atmosphere from combustion or from wind erosion of contaminated surface soils.

In summary, published investigations to date indicate that:

1. 2,3,7,8-TCDD undergoes relatively rapid photolysis in sunlight when dissolved in solution.
2. The rate of photolysis is dependent on the chemical microenvironment; organic solvents greatly accelerate the photolysis.

3. Photolysis of 2,3,7,8-TCDD in soils is slow, and was not observed in several studies: addition of an organic solvent to the soils promotes the photolysis.
4. Information on how soil properties affect the photolysis is lacking. Also, the depth dependence of photolysis is not well understood.
5. Successful modeling of 2,3,7,8-TCDD photolysis in soils requires additional basic information on the significance of photolysis in relation to other fate and transport processes.

Transport Processes

2,3,7,8-TCDD and related compounds are transported while sorbed on particles, while dissolved in water or other solvents, or while dispersed in the vapor state. If photolysis is the primary pathway for detoxication of TCDD, transport to sunlight exposed areas may be the limiting factor for degradation, especially in soils where vertical transport of 2,3,7,8-TCDD is exceedingly slow. Its extremely low water solubility and vapor pressure combine to give a rate of movement expressed in cm/year in soils (22), although added organic solvents can greatly increase the mobility of TCDD. Consequently, estimating the rate of movement of 2,3,7,8-TCDD in soils requires detailed data on the soil characteristics and the presence of solvents or oils.

The reported log octanol-water partition coefficient (K_{ow}) for 2,3,7,8-TCDD varies from 6.15 to 8.48 (3,7,8). The magnitude of this value, in addition to the low water solubility, suggests that it will be primarily associated with particles in sediment and soil, with a vanishingly small fraction in the non-sorbed phase. This was demonstrated by Jackson and coworkers (46) who examined the solubility of 2,3,7,8-TCDD in ten soils. They observed that the soil partition coefficient for ten soils ranged from 0.4×10^5 to 45.8×10^5. Although 2,3,7,8-TCDD would move only very slowly in these soils, if oils or other solvents were present, movement may be more rapid.

Volatilization of 2,3,7,8-TCDD from soils is expected to be very slow, due to the low vapor pressure and high octanol-water partition coefficient. Mill (47) estimates that the half-life for vaporization of 2,3,7,8-TCDD from soils will range from many months to years, in the absence of intervening transformation processes. Due to this rather substantial period, and the observed relatively rapid photolysis on soils, vaporization from soils may not be a significant source of 2,3,7,8-TCDD in the atmosphere. The main source of cholorinated dibenzodioxins in the atmosphere is probably municipal and industrial incineration (10). Because of large partition coefficients, dioxins in the atmosphere are likely associated predominantly with particles. Further information is needed, however, to firmly resolve the physical state of dioxins in the atmosphere.

In the top several centimeters of soil, photolysis, volatilization, mass transport in water either dissolved, sorbed on particles, or complexed with other molecules, and bioturbation are potential processes that affect chemical behavior. Freeman and Schroy (22) have developed a model for movement of 2,3,7,8-TCDD in soils based

on volatilization as the predominant transport process. To simulate the effect of temperature on the transport of 2,3,7,8-TCDD in soil, a time dependent energy balance model was constructed. Using this model they calculated the expected movement of 2,3,7,8 TCDD at a site at Eglin Air Force Base that had been intentionally contaminated 12 years previously at a depth of 11 cm. Careful analysis of the various depths of the soil indicated that 2,3,7,8-TCDD had dispersed approximately 10 cm during the 12-year period. Agreement was found between the model results and the observed depth profile.

Podoll and coworkers (3) have redetermined the vapor pressure of 2,3,7,8-TCDD. Using this information together with the aqueous solubility, octanol/ water partition coefficient and photolysis quantum yields, investigators have estimated the half-lives for movement and transformation of 2,3,7,8-TCDD in water and air. Even though the vapor pressure (P) of 2,3,7,8-TCDD is low, the water solubility (S) is also very low and the Henry's law constant is therefore significant, and allows vaporization from water.

$$H = P/S = 7.4 \times 10^{-10} \text{ torr}/6 \times 10^{-11} \text{ M}$$

$$= 12 \text{ torr M}^{-1}$$

Using a two film model, the volatilization half-lives for 2,3,7,8-TCDD were estimated to be 32 and 16 days, respectively, in 200 cm deep ponds and rivers.

Concluding Comments

2,3,7,8-TCDD is the most toxic of the dioxins and remains a primary concern for exposure to humans. Although combustion sources of this compound are now readily accepted, waste contaminated soils and waste dumps remain a costly problem.

The extensive amount of research on this compound has indicated that 2,3,7,8-TCDD is both remarkably stable and is almost exclusively associated with particulate material. Because of the low water solubility and high sorption on soils, it moves only very slowly in natural soils. Human exposure to 2,3,7,8-TCDD in soils is thus a function of movement and degradation (primarily photochemical) on soil particles. Enhanced movement of 2,3,7,8-TCDD in soils also contaminated with oils and/or solvents potentially can increase concentrations near the surface, and this process, along with photolysis on particles, requires further investigation.

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